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Determination of Absolute f Values from Relative Intensity Measurements for Spectral Lines with Doppler Contour*

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THE experimental determination of absolute intensities for isolated spectral lines or for entire vibration-rotation bands involves formidable experimental difficulties. For this reason it is highly desirable to consider the use of techniques which permit the *determination of absolute f values from relative intensity measurements* performed by the use of a low resolution spectrograph. It is the purpose of this note to call attention to a useful experimental procedure for spectral lines with Doppler contour and for optical densities which are sufficiently large to assure a nonlinear dependence of intensity on optical density. The method is a generalization of a two-path experiment proposed for emission studies on flames.[1]

For spectral lines with Doppler contour it is well known[2] that the total absorbed intensity of radiation $A[\nu_{lu}(K)]$, for the line identified by the index K and with center at the frequency ν_{lu}, is

$$A[\nu_{lu}(K)]\simeq R^0(\nu_{lu})(mc^2/2\pi kT\nu_{lu}^2)^{-\frac{1}{2}}[P_{\max}(K)X]\times\left\{\sum_{n=0}^{\infty}[(n+1)^{\frac{1}{2}}(n+1)!]^{-1}[-P_{\max}(K)X]^n\right\}, \quad (1)$$

if $R^0(\nu_{lu})$ is the intensity of the incident radiation at ν_{lu}, m is the mass of the absorber, c equals the velocity of light, k is the Boltzmann constant, T represents the absolute temperature, X is the optical density (in cm-atmos) of the absorber, and $P_{\max}$ is the maximum value of the spectral absorption coefficient (in cm^{-1}-$atmos^{-1}$). The quantity $P_{\max}$ is related to the integrated intensity S (in cm^{-2}-$atmos^{-1}$) through the relation

$$P_{\max}=S(mc^2/2\pi kT\nu_{lu}^2)^{\frac{1}{2}};$$

the quantity S (in cm^{-2}-$atmos^{-1}$) is related to the dimensionless f value through the expression

$$S=2.3789\times10^7(273.1/T)f.$$

It is apparent from Eq. (1) that the dimensionless ratio $R=A[\nu_{lu}(K)]/R^0(\nu_{lu})(mc^2/2\pi kT\nu_{lu}^2)^{-\frac{1}{2}}$ is a unique function[2] of $P_{\max}X$, i.e., $R=\varphi(P_{\max}X)$. If $R=R_1$ for $X=X_1$ and $R=R_2$ for $X=X_2$, then $R_1/R_2=\varphi(P_{\max}X_1)/\varphi(P_{\max}X_2)=\varphi^1(P_{\max}X_1, X_1/X_2)$. The function φ^1 can be determined without difficulty for arbitrary values of X_1/X_2. For $X_1/X_2=2$ the results have been published elsewhere.[1] From the known values of X_1/X_2 and the measured values of R_1/R_2 it is a simple matter to obtain $P_{\max}X_1$ and hence P_{max} or S. In this manner absolute f values can be determined from relative intensity measurements for spectral lines with Doppler contour.

For studies in the visible and ultraviolet regions of molecular spectra, and at ordinary temperatures, $h\nu_{lu}\gg kT$ and[1]

$$\frac{\partial\ln\{P_{\max}(K)X/[g_u(q_{lu})^2]_K\}}{\partial(E_u-h\nu_{lu})}=-1/kT, \quad (2)$$

where $g_u(q_{lu})^2$ represents the relative transition probability for the line with index K, E_u is the energy of the upper state, and h is Planck's constant. At fixed values of T, Eq. (2) is useful for checking the consistency of experimentally determined values of $P_{\max}(K)X$.

The two-path absorption experiments can be generalized to spectral lines with combined Doppler- and collision-broadening if the line shape is known or is to be measured.

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[2] R. Ladenburg, Z. Physik **65**, 200 (1930).